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Thermal Conductivity Measurements of Caged Structural Superconductors

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Abstract

Thermal conductivity of $Ca_3Rh_4Sn_{13}$ and $Sr_3Ir_4Sn_{13}$ were measured in magnetic fields to reveal superconducting state. From magnetic susceptibility $\chi(T)$ and electrical resistivity $\rho(T)$ measurements, superconducting transition temperature T_c of $Ca_3Rh_4Sn_{13}$ and $Sr_3Ir_4Sn_{13}$ is determined to be 8 and 5 K, respectively. Thermal conductivity $\kappa(T)$ of $Ca_3Rh_4Sn_{13}$ indicates that superconducting state is nodeless *s*-wave, because residual thermal conductivity κ_0/T in zero magnetic field is very small. On the other hand, $\kappa(T)$ of $Sr_3Ir_4Sn_{13}$ in zero magnetic field suggests that superconductivity possesses nodal gap rather than full gap. Whether nodal superconducting gap exists or not still remains to be clarified, because there is a possibility that the achieving temperature is insufficient to discuss superconducting state.

Keywords: superconductor; thermal conductivity; caged structure

1. Introduction

Since thermal conductivity is known to be sensitive to quasiparticles of low energy excitation, thermal transport measurements are useful for the studies of superconducting state. For example, the thermal conductivity measurements for a heavy-fermion superconductor UPt_3 show the crucial information on the symmetry of the superconducting gap [1, 2]. Since the symmetry of superconducting gap is deeply involved with the origin of the superconductivity, the thermal conductivity measurements give us a significant information on superconducting gap symmetry.

$R_3Tr_4Sn_{13}$ (R = rare earth or alkaline earth metal, Tr = transition metal) is attracted attention in the field of solid state physics, because of the existence of charge density wave (CDW) and a quantum phase transition in superlattice [3]. $R_3Tr_4Sn_{13}$ has a cubic structure with the space group *Pm-3n* (No. 223) and caged structure. Twelve Sn atoms form icosahedra and surround one Sn atom at the center. A humpy anomaly is observed in electrical resistivity and magnetic susceptibility measurements for $Ca_3Ir_4Sn_{13}$, $Sr_3Tr_4Sn_{13}$ (Tr = Rh, Ir) near $T^* \sim 33$, 137 and 147 K, respectively [3-7]. With a single crystal $Sr_3Ir_4Sn_{13}$, X-ray diffraction measurement proves the structure transition *I* phase (*Pm*-3*m*) to *I*' phase (*I*-43*m*) [3]. The structure transition leads to a distortion of the structure and a formation of a superlattice associated with CDW. In the case of a coexistence of superconducting and CDW, the caged compound is expected to have unconventional superconductivity. To reveal the

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superconducting state of $R_3Tr_4Sn_{13}$, several measurements have been performed. Specific heat measurements on $R_3Tr_4Sn_{13}$(R = Ca, Sr, La; Tr = Co, Ir, Rh) indicate nodeless superconductivity [8 - 11]. Thermal conductivity measurements suggest that $Ca_3Ir_4Sn_{13}$ has nodeless gap [12]. Penetration depth measurements on $Sr_3Ir_4Sn_{13}$ indicate a single *s*-wave or a two-gap *s* + *s*-wave superconductivity state [13].

$Ca_3Rh_4Sn_{13}$ shows the superconducting transition temperature T_c ~ 8.6 K with the upper critical field $\mu_0H_{c2}(0)$ ~ 4 T[14] and $Sr_3Ir_4Sn_{13}$ has T_c ~ 5 K with $\mu_0H_{c2}(0)$ ~ 3.5 T[10]. There are few reports of the superconducting gap symmetry of $Ca_3Rh_4Sn_{13}$ and $Sr_3Ir_4Sn_{13}$. In this article, we report the result of thermal conductivity measurements of $Ca_3Rh_4Sn_{13}$ and $Sr_3Ir_4Sn_{13}$ to reveal superconducting gap symmetry.

2. Experiment details

We prepared single crystals of $Ca_3Rh_4Sn_{13}$ and $Sr_3Ir_4Sn_{13}$ by a Sn self-flux method [10]. Sr (Ca) chips, Ir (Rh) and Sn grains were mixed in an atomic ratio of 2.5:1:40 in a glove box. The mixture was sealed in an evacuated quarts tube. The tube was heated up to 1050 °C, kept for 3 h, then cooled down to 500 °C for 90 h. The excess Sn was separated by a centrifuge. Small amount of residual Sn-flux on the crystal surfaces were removed by 10 % hydrochloric acid. The crystal structure of the single crystal was examined by powder-X-ray diffraction (XRD). The samples of $Ca_3Rh_4Sn_{13}$ and $Sr_3Ir_4Sn_{13}$ were shaped to 2.3 × 0.5 × 0.5 mm^3 and 1.7 × 0.4 × 0.4 mm^3, respectively. Four gold wires were attached to the sample with spot welding and sintered silver paste. DC magnetic susceptibility $\chi(T)$ were carried out by MPMS (Quantum Design) down to 2 K. Electrical resistivity $\rho(T)$ and thermal conductivity $\kappa(T)$ measured in a ^{3}He cryostat (Oxford Heliox VL) down to 0.28 K. The thermal conductivity were measured by a steady-state method with one-heater and two-thermometer (RuO_2). Magnetic field was applied to [100], and perpendicular to the heat current along [100].

3. Results and Discussion

Figure 1(a) shows T-dependence of the magnetic susceptibility $\chi(T)$ for $Ca_3Rh_4Sn_{13}$ in a magnetic field of 1 mT. The sharp superconducting transition occurred at T_c^{onset} = 8.3 K. This value is in good agreement with the previous report [14]. The Meissner volume fraction is estimated to be ~100 %, strongly indicating that superconductivity is of bulk nature. Figure 1(b) shows T-dependence of the electrical resistivity $\rho(T)$ for $Ca_3Rh_4Sn_{13}$. The $\rho(T)$ behavior is similar to that of a caged compound KOs_2O_6 [15]. Inset of Fig. 1(b) shows $\rho(T)$ below 15 K. The zero resistivity was observed at 8.0 K. The residual resistivity ρ_0 was obtained to be 12.9 μΩcm, by means of extrapolation to 0 K of $\rho = \rho_0 + AT^2$. The residual resistivity ratio [RRR = ρ(300 K)/ρ_0] was estimated to be approximately 13. The $\rho(T)$ of $Sr_3Ir_4Sn_{13}$ revealed superconducting transition at 5 K. The ρ_0 was obtained to be ρ_0 = 8.37 μΩcm by means of extrapolation to 0 K of $\rho = \rho_0 + AT^2$ (not shown in this article). The behavior of $Sr_3Ir_4Sn_{13}$ is corresponding to that in the previous report [10].

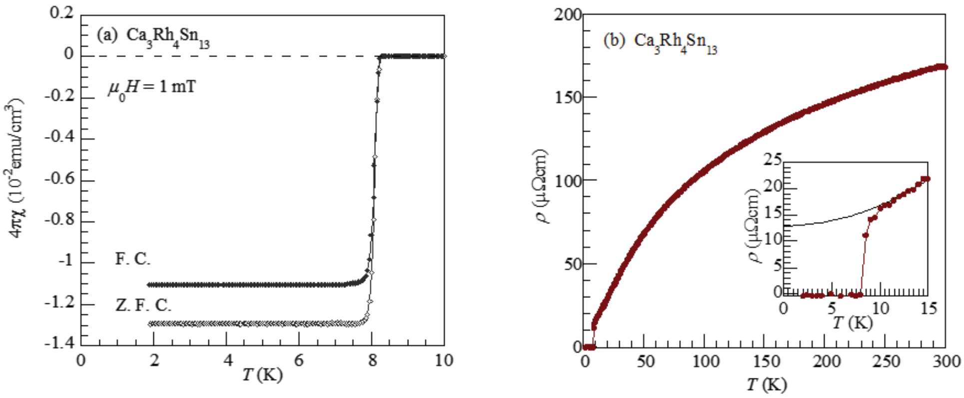

Fig. 1. (a) T-dependence of the magnetic susceptibility $\chi(T)$ of $Ca_3Rh_4Sn_{13}$ in a magnetic field of 1 mT. (b) T-dependence of the electrical resistivity $\rho(T)$ of $Ca_3Rh_4Sn_{13}$. The inset shows $\rho(T)$ around superconductive transition. The solid line is the fitting result of $\rho = \rho_0 + AT^2$.

Figure 2 shows T-dependence of the thermal conductivity $\kappa(T)$ divided by T of $Ca_3Rh_4Sn_{13}$ in magnetic fields of 0 and 5 T versus T^2. The measured thermal conductivity $\kappa(T)$ includes electron and phonon contributions. The data was fitted by $\kappa(T)/T = a + bT^{2.2}$ below 0.5 K, where a (= κ_0/T) is a residual term extrapolated to T = 0 K. The κ_0/T is electron contribution and the power term is phonon contribution. The fitting of $Ca_3Rh_4Sn_{13}$ gave a = 11 μW/K^{2}cm. The residual term of the nodeless superconductors approaches zero because of an absence of quasiparticles excited in low energy. The small value of a at 0 T of $Ca_3Rh_4Sn_{13}$ suggests that superconducting gap is nodeless *s*-wave. The result is consistent with that obtained from specific heat measurements [11], and is very similar to that of $Ca_3Ir_4Sn_{13}$ [12]. In normal state, the value of a at 5 T was obtained to be 1.64 mW/K^{2}cm. With the Lorenz number L_0 = 2.45 $\times 10^{-8}$ WΩ/K^{-2} and the residual electrical resistivity ρ_0, the Wiedemann-Franz law gave L_0/ρ_0 = 1.87 mW/K^{2}cm. The Wiedemann-Franz law can be expressed to be $\kappa_0/T = L_0/\rho_0$ in normal state. The value of a at 5 T disagrees with L_0/ρ_0. Since T_c is relatively high, the $\rho(T)$ measurements in magnetic fields above $\mu_0 H_{c2}(0)$ are needed to estimate the proper value of ρ_0.

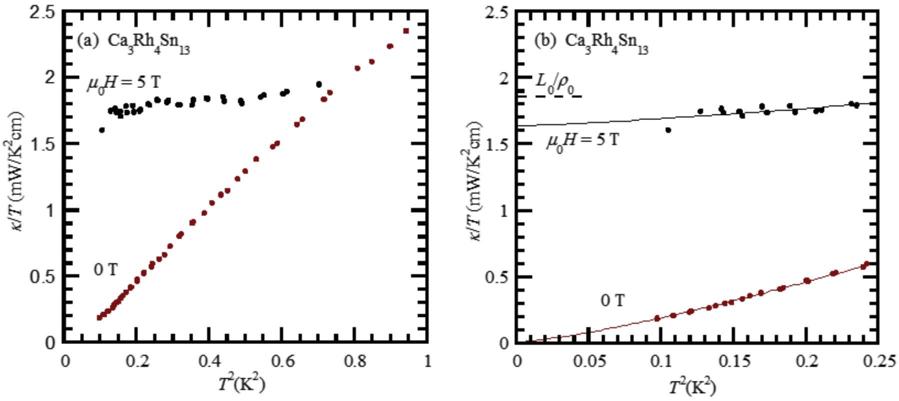

Fig. 2. (a) T-dependence of κ/T of $Ca_3Rh_4Sn_{13}$ in magnetic fields of 0 and 5 T. (b) κ/T of $Ca_3Rh_4Sn_{13}$ at low temperature region. The dashed line is the normal-state the Wiedemann-Franz law L_0/ρ_0. The solid line represents the fitting result of $\kappa/T = a + bT^{2.2}$.

Figure 3 shows thermal conductivity $\kappa(T)$ divided by T of $Sr_3Ir_4Sn_{13}$ in magnetic fields of 0 and 2 T versus T^2. The data can be fitted well with $\kappa(T)/T = a + bT^{2.6}$ below 0.5 K. The value of a at 0 T was evaluated to be 0.606 mW/K^{2}cm. The value seems to be relatively large, suggesting nodal superconducting gap. However specific heat and penetration depth measurements suggest that $Sr_3Ir_4Sn_{13}$ has nodeless gap in the previous reports [10, 13]. One of the origins of the disagreement is that an achieving temperature is insufficient to discuss superconducting state ($T/T_c \sim 0.06$). By clarifying the value of a at 0 T of $Sr_3Ir_4Sn_{13}$, it is possible to reveal whether node exists in superconducting gap or not, by means of measurements at lower temperatures. In the magnetic field of 2 T, the value of a was obtained to be 3.14 mW/K^{2}cm. With the residual electrical resistivity ρ_0 = 8.37 μΩcm, the Wiedemann-Franz law gave L_0/ρ_0 = 2.93 mW/K^{2}cm. The value of a at 2 T disagrees with L_0/ρ_0, because superconductivity still remains in the magnetic field of 2 T. The $\kappa(T)$ measurements is required in higher magnetic fields which exceeds $H_{c2}(0)$ of 3.5 T.

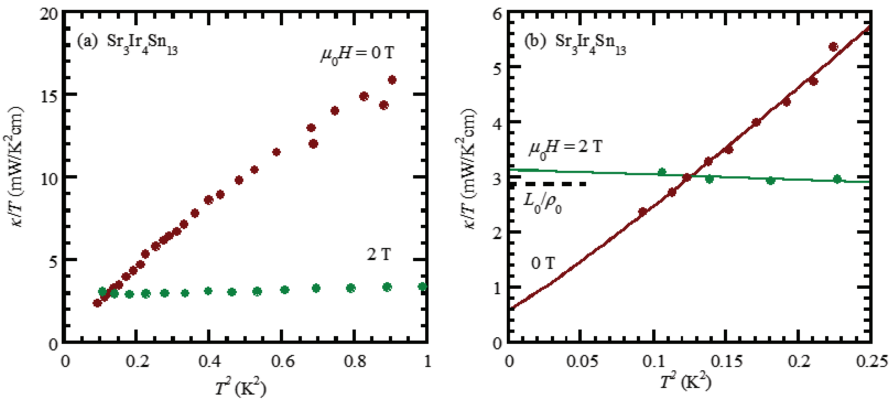

Fig. 3. (a) T-dependence of κ/T of $Sr_3Ir_4Sn_{13}$ in magnetic fields of 0 and 2 T. (b) κ/T of $Sr_3Ir_4Sn_{13}$ at low temperature region. The dashed line is the normal-state Wiedemann-Franz law L_0/ρ_0. The solid line represents the fitting result of $\kappa/T = a + bT^{2.6}$.

4. Conclusion

We succeeded in synthesizing the single crystal of $Ca_3Rh_4Sn_{13}$ and $Sr_3Ir_4Sn_{13}$ by a Sn-flux method. By using the single crystal, we performed magnetic susceptibility $\chi(T)$, electrical resistivity $\rho(T)$ and thermal conductivity $\kappa(T)$ measurements. The behavior of $\rho(T)$ of $Ca_3Rh_4Sn_{13}$ is similar to a caged compound KOs_2O_6 [15]. T_c of $Ca_3Rh_4Sn_{13}$ was observed in 8.3 K. The $\kappa(T)/T$ of $Ca_3Rh_4Sn_{13}$ seems to approach zero. The behaviour of $\kappa(T)$ suggests that $Ca_3Rh_4Sn_{13}$ is a nodeless superconductor. The results of $Ca_3Rh_4Sn_{13}$ is very similar to that obtained from the previous works [11]. Thermal conductivity of $Sr_3Ir_4Sn_{13}$ implies nodal superconductivity, rather than full gap. However, the result is different from those of the previous reports [10, 13]. We have to treat carefully about whether nodal superconducting gap exists or not. This is because there is a possibility that the achieving temperature is insufficient to discuss superconducting state. Lower temperature measurements with a dilution refrigerator are now in progress.

Acknowledgements

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